KAOLINITES AS DOSIMETERS : A NEW POSSIBILITY OF TRACING RADIONUCLIDES MIGRATION

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Natural minerals often exhibit native radiation damage which can be investigated by a variety of methods : thermoluminescence and Electron Paramagnetic Resonance (EPR) for defect centers, fission tracks... In most minerals, radiation damage arises from radionuclides trapped during growth and provides few informations on the environmental geochemistry prevailing after crystal growth. A notable exception concerns the surface radiation damage observed in some minerals (e.g. coatings on quartz and diamond). Clay minerals present over other minerals the advantage of a large specific surface which allows an efficient interface with solutions and make them sensitive to the environment, even after crystal growth. The specific advantage of kaolinite resides in its presence in a wide range of geological environments, including low temperature alteration of granites and tuffs, surficial weathering and sedimentary rocks. Indeed all natural kaolinites show a significant concentration of defect centers which correspond either to background or anomalous irradiation during or after growth. The purpose of this presentation is twofold: (i) simulation of natural radiation and thermal annealing in order to derive the EPR signal intensity vs. dose rate relationship used in a kaolinite-based dosimetry; (ii) application in natural systems to the migration of short-lived radionuclides, in relation with uranium exploration.

PARAMAGNETIC DEFECT CENTERS IN KAOLINITES

EPR spectra of natural kaolinites exhibit a complex signal arising from the presence of different defect centers, in addition to signals due to paramagnetic impurities (mostly Fe^{3+}). The structure of these radiation-induced defect centers as well as their thermal stability has been investigated in order to understand the effect of external radiations on the creation of paramagnetic centers and their persistance with time. Three centers are clearly separated on EPR spectra, when the frequency of the spectrometer is correctly selected. Two of them are positive holes associated to silicon, the other one is a hole associated with aluminum. They have distinct thermal stability, according to isochronal heating experiments. The first positive hole associated to silicon is stable over geological periods (10^6-10^8 years at low temperatures) and is indeed observed in all natural kaolinites. The two other centers are observed only in kaolinite samples submitted to recent irradiation, owing to their fast annealing over geological times and moderate temperatures. In uranium deposits, it is thus possible to separate the irradiation arising from recent remobilization of short lived radionuclides from that due to the emplacement of uranium mineralization, making this a unique tool for tracing the dynamics of radionuclides transfer.

DOSE RATE ESTIMATION

We have used four radiation sources : calibrated x-rays (Mo-tube), γ-rays (^{60}Co source) and ion implantation (He^+ and Pb^{++}) in order to simulate the natural radiation. We have determined for each irradiation the kind of paramagnetic centers created as well as their total concentration. Various kaolinite samples have been chosen, representing

different formation conditions (hydrothermal alteration, weathering, sedimentary rocks) : the irradiation has been found to decorate pre-existing diamagnetic centers and the EPR response is thus sample-dependent, with some influence of the crystallinity and iron content of kaolinite crystals. For each sample the relation linking the radiation dose and the EPR signal intensity has been derived. The relative efficiency of the various sources employed has been carefully investigated; for instance, α-radiation seems the most efficient. Isothermal heating at various temperatures shows that paramagnetic defect formation is not a first order process. Approximate activation energies have been obtained.

USE OF KAOLINITES AS "IN SITU" DOSIMETERS

The knowledge of the parameters governing the formation and the stability of the radiation centers in kaolinites allows to use this mineral as a dosimeter. In the finely divided clay minerals, the surface reactions with percolating solutions are greatly enhanced : the radiation damage arises from external irradiations. The accumulated dose rate is calculated from the dosimetry experiments by extrapolating to zero-EPR signal intensity. It may be further converted to the total quantity of the suspected radionuclides if some constraints are put on the age of the irradiation. We have tested this potential use on various alteration systems associated with uranium concentrations as well as in environments devoid of major radionuclide transfers. Kaolinites sampled in two profiles from a brazilian laterite developped on U-mineralized albitite and on associated non-mineralized gneiss show a relationship between defect center and total uranium content. Another example has been chosen in a tropical soil from Cameroon and has shown that the accumulated dose is larger than the present uranium concentration by 2 to 3 orders of magnitude, indicating a non-equilibrium U-decay system during all the period of soil differentiation.

Kaolinites associated to uranium concentrations allow to trace the path of past transfer of shortlived radionuclides and reveal the dynamics of the system during alteration. In both cases the informations are complementary to the present day geochemical analyses which are only sensitive to the parts of the rock in which the radionuclides have been "blocked".